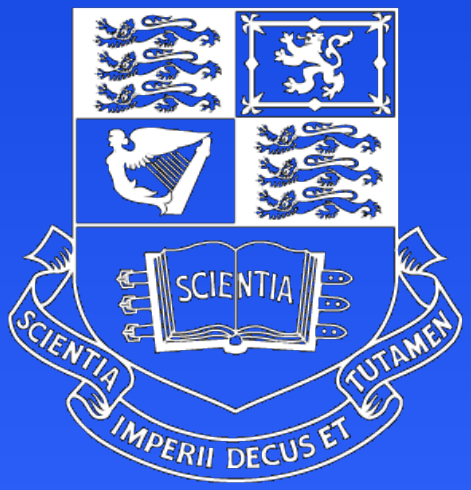
# Solid Polymer Fuel Cell research at Imperial College




***Dr Anthony Kucernak***

**Interfacial Science Group**

**Department of Chemistry**

**Imperial College of Science, Technology & Medicine**

**London SW7 2AZ, UK**

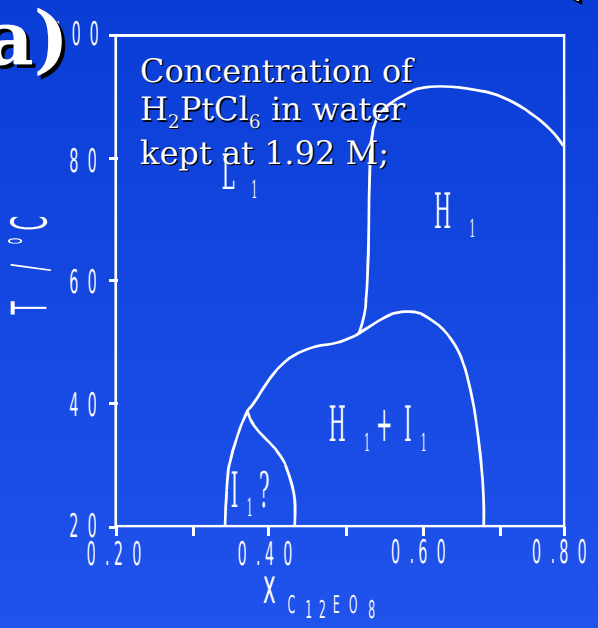
a.kucernak@ic.ac.uk

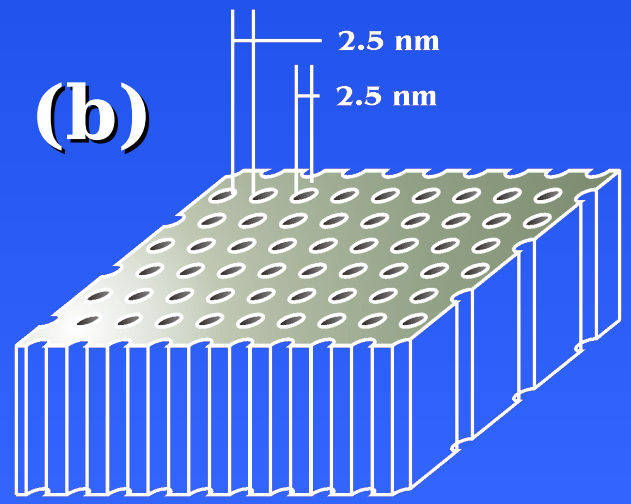
# Areas of specialisation

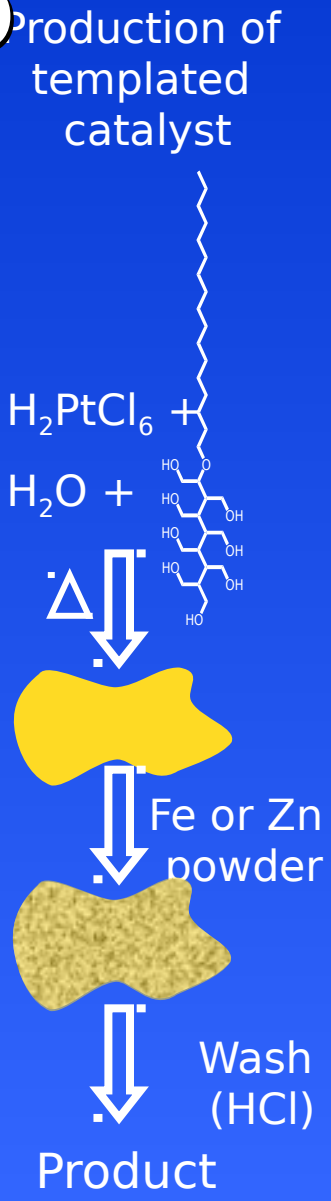
- New electrocatalysts
  - New catalysts based on nanoparticulate Au for CO clean-up and oxidation of new fuels;
  - New types of catalysts produced through templating mechanisms;
- New approaches to characterise electocatalysts
  - Copper underpotential deposition gives the TRUE surface composition of catalysts used in reformate-tolerant and direct methanol fuel cells (DMFC);
  - Nanoelectrode studies allow the study of a single electrocatalyst
- New membrane materials for high temperature and DMFC
  - Lower permeability towards methanol;
  - High unpressurised operating temperature (120-140◦C);
- New approaches to structure the catalyst/membrane interface
  - Development of techniques and computer simulation approaches to enable the design of the fuel cell catalyst layer (c.f.current empirical approaches)
- New *in situ* techniques for studying and fuel cells
  - New hardware approaches to look at the real-time current, temperature and product distribution within operating fuel cells;
  - Development of computer simulation packages to evaluate results

# New Electrocatalysts

- Based on templated precious metals;
- Phase diagram, (a), shows production of liquid-crystalline phases ($H_I$, and $I_I$);
- Bulk morphology looks like a bulk metal with “holes drilled through it”, (b);
- Method of production is very simple and utilised metal powder as a reductant, (c).

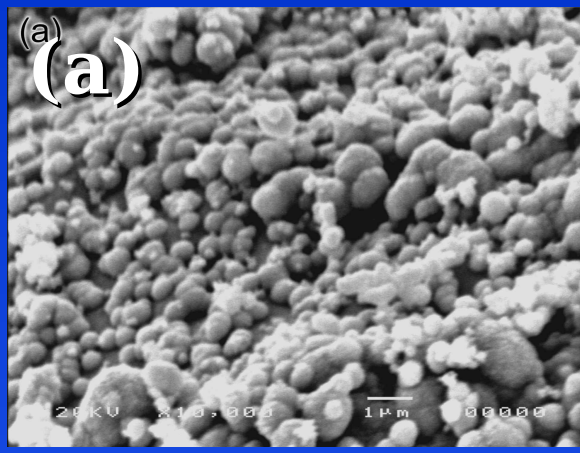


# Morphology and activity

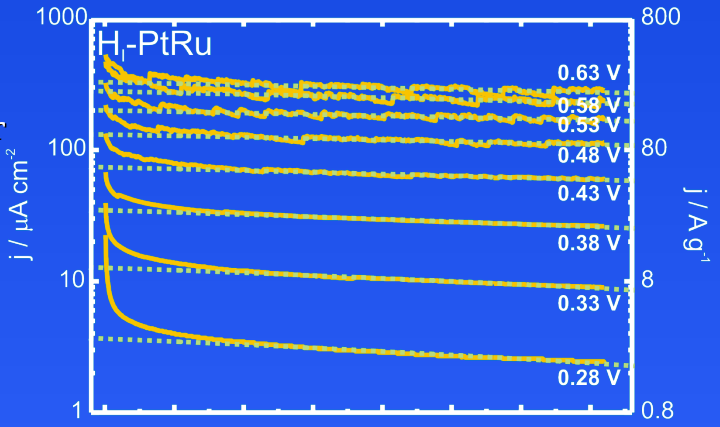
- Bulk morphology looks like a low surface area powder, (a), but high resolution TEM shows that particles are porous, (b) ;
- Catalysts show very good activity to oxygen reduction and the oxidation of organic fuels, and are good catalysts for the DMFC, (c)

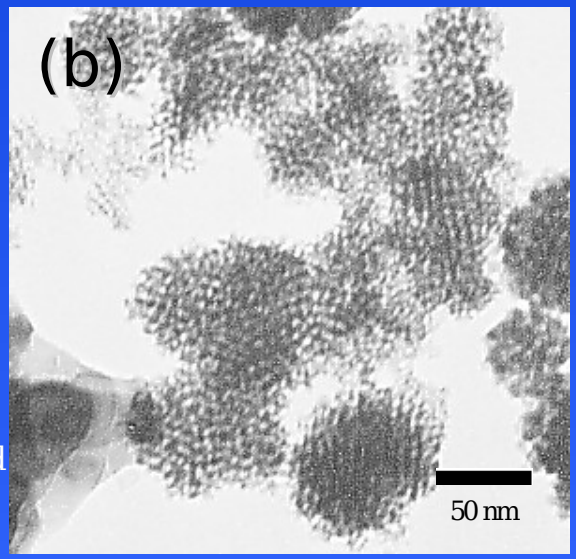



SEM image of material (a) shows particles with radii in 0.1-1 μm range

**(c)**

Chronoamperometric response to methanol oxidation at different potentials; 0.5 mol $dm^{-3}$ $H_2SO_4$ + 0.5 mol $dm^{-3}$ methanol at 60 °C.



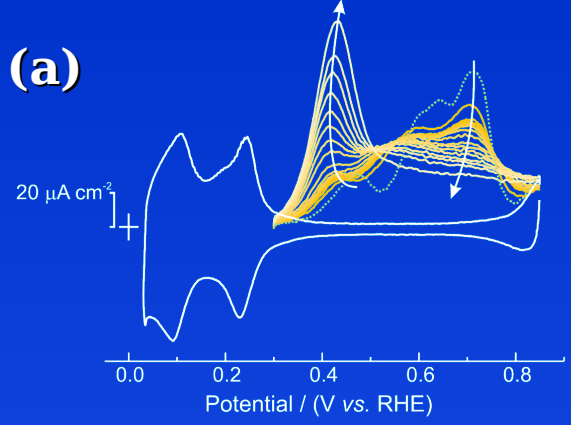

TEM image, (b), shows Pt are porous with holes 2.7±0.2 nm in diameter separated by 2.7±0.2 nm walls.

**References**

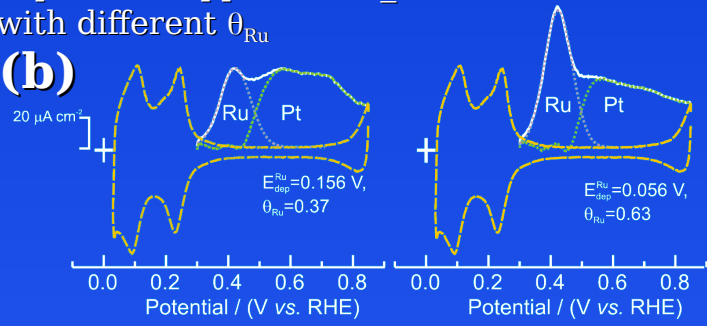

1. J. Jiang, A. Kucernak, "Oxygen reduction studies of templated mesoporous platinum catalysts", Electrochem. Solid. State Lett., 3 (2000), pp. 559-562
2. J. Jiang and A. Kucernak, "Nanostructured platinum as an electrocatalyst for the electrooxidation of formic acid", J. Electroanal.Chem., 520(2002),64-70
3. J. Jiang and A. Kucernak, "Electrooxidation of small organic

# New approaches to characterise electocatalysts

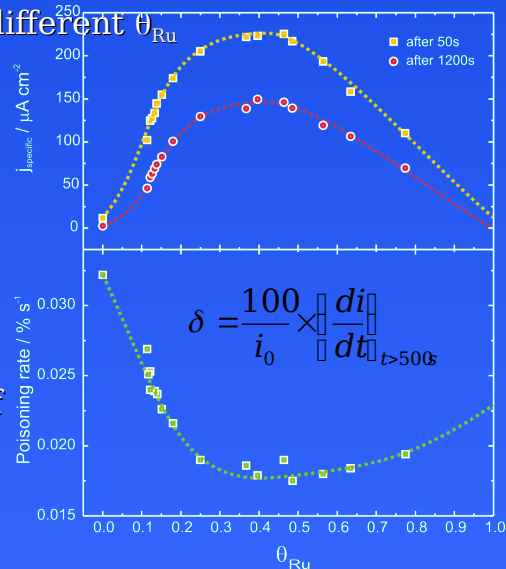
- We have developed new techniques to monitor the surface compostion of a catalyst *in situ*, and thus determine the optimium surface composition;
- The technique involves the deposition of a monolayer of copper. As the copper deposits differently on Pt from Ru, we can deconvolute the amount of Pt and Ru on the surface;
- We can use this technique to monitor the activity of various reactions as a function of surface composition. (c)




Stripping voltammetry of undepotentially deposited copper on Pt_Ru electrodes with different $\theta_{Ru}$




Deconvolution of Pt and Ru surface area for Pt-R electrodes with different $\theta_{Ru}$



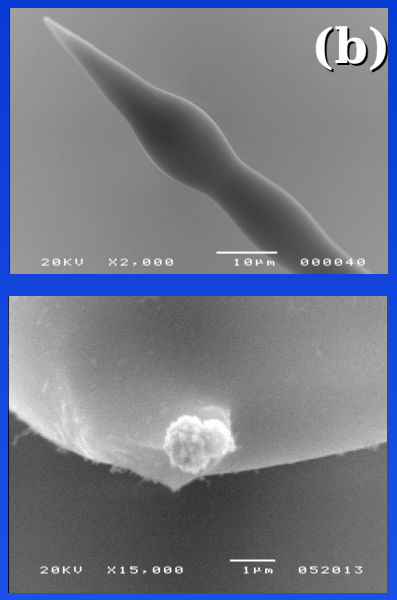

Variation in activity towards methanol oxidation as a function of $\theta_{Ru}$


**References**

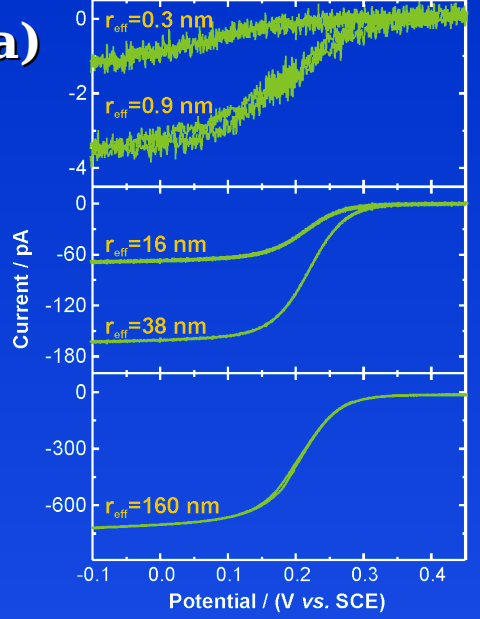
1. C.L. Green, A. Kucernak, "Determination of the platinum and ruthenium surface areas in platinum-ruthenium alloy electrocatalysts by underpotential deposition of copper. I. Unsupported catalysts, *J. Phys. Chem. B,* 106 (2002), 1036-1047.
2. C.L. Green, A. Kucernak, "Determination of the platinum and ruthenium surface areas in platinum-ruthenium alloy electrocatalysts by underpotential

# New approaches to characterise electrocatalysts

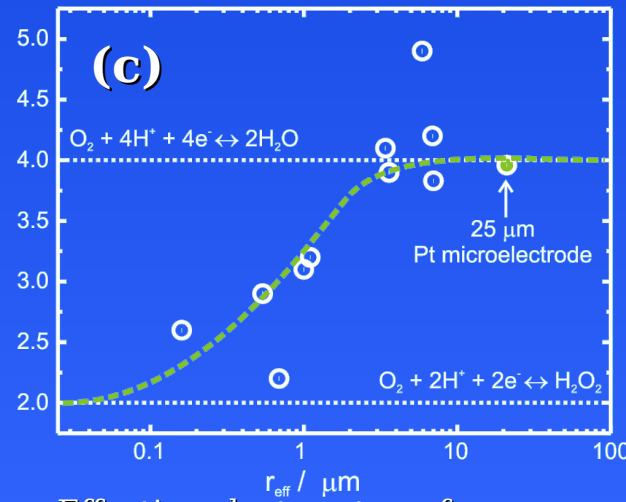
- Development of ultra-small carbon nanoelectrodes, (a);
- Deposition of ultra-small Pt particles on those electrodes, (b);
- Monitoring of reactions of interest, for instance, oxygen reduction, on these electrodes as a function of particle size, (c).
- There are strong indications that the loss of peroxide occurs under conditions of high mass transport.




SEM images of an insulated carbon nanoelectrode (top), and a large Pt particle grown on the Carbon electrode (bottom).




Limiting current for carbon nanoelectrodes of different sizes in 0.01 mol $dm^{-3}$ $K_3Fe(CN)_6$ + 0.5 mol $dm^{-3}$ KCl, 10 mV $s^{-1}$.




Effective electron transfer number, *n*, as a function of Pt particle size indicating the

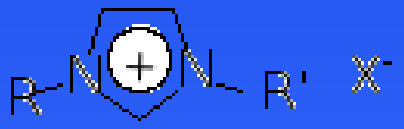

**References**

1. S Chen, A. Kucernak, "Fabrication of carbon microelectrodes with an effective radius of 1 nm", *Electrochem. Comm.*, 4(2002), 80-85.
2. S Chen, A. Kucernak, "The voltammetric response of nanometer-sized carbon electrodes", *J. Phys. Chem. B.*, submitted.

# New polymeric proton conductors

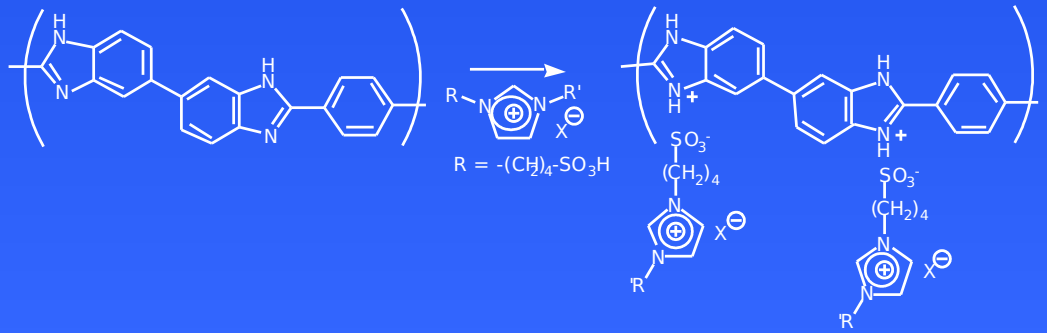
- Develop methanol-excluding membranes for the DMFC with the following properties:
  - Ionic conductivity greater than 0.02 S $cm^{-1}$ – necessary so that we do not have large iR losses;
  - Ability to operate at up to 140°C – to improve kinetics, and enable better heat rejection from the fuel cell;
  - Little or no dependence on water to provide the proton conduction mechanism;
- Approach is to base membrane materials on immidazolium-type structures (a);
- Through this the approach is to produce polyelectrolytes doped with ionic liquids carrying an acidic functionality, (b).

**(a)**



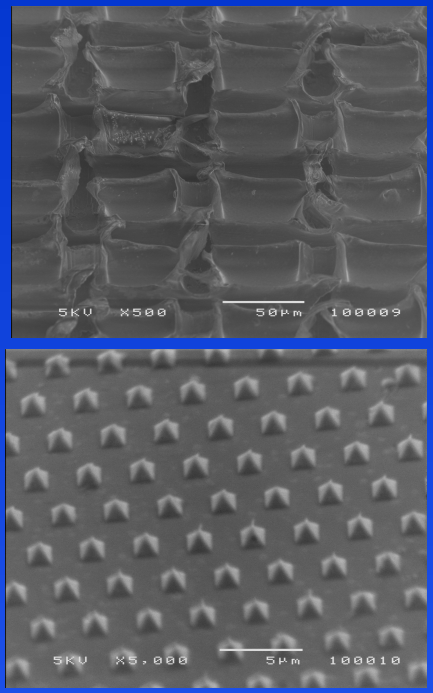
R, R' =H, Me, Et, Pr..
X =OTf, $NTf_2$ $CTf_3$

**(b)**

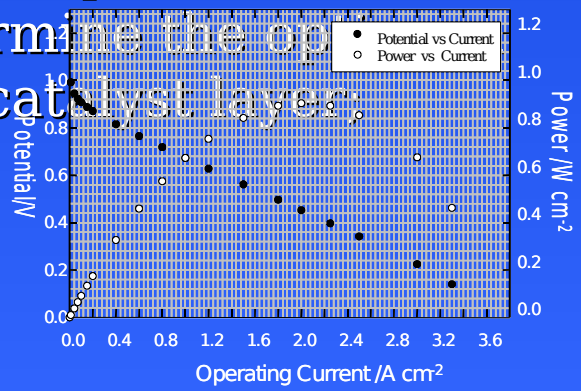


# New approaches to structure the catalyst/membrane interface

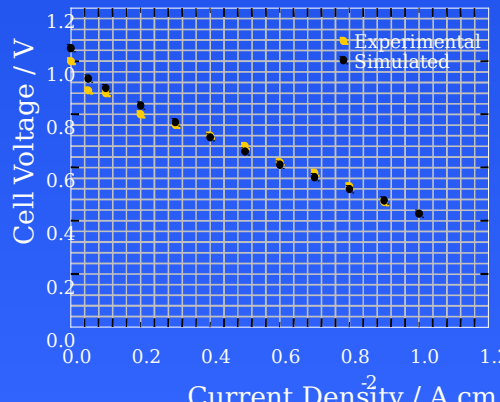
- Design MEA from ground up, including the catalyst layer and the structure of the interface;
- Use polymer precursors to produce membrane during manufacture, (a);
- Utilise sputter deposition of catalyst to produce high surface area thin interfacial catalyst layer
- Model the effects of different geometries of the 3-phase contact area, (c), to determine the optimum geometry of the catalyst layer.




(a) SEM images of structured Nafion interfaces




(b) Simulated and actual response




**References**

1. R. Wang, A. Kucernak, "Modelling the conditions and composition within a PEM fuel cell to optimise performance I. Optimising composition of the catalyst layer", *J. Electroanal. Chem.*, submitted

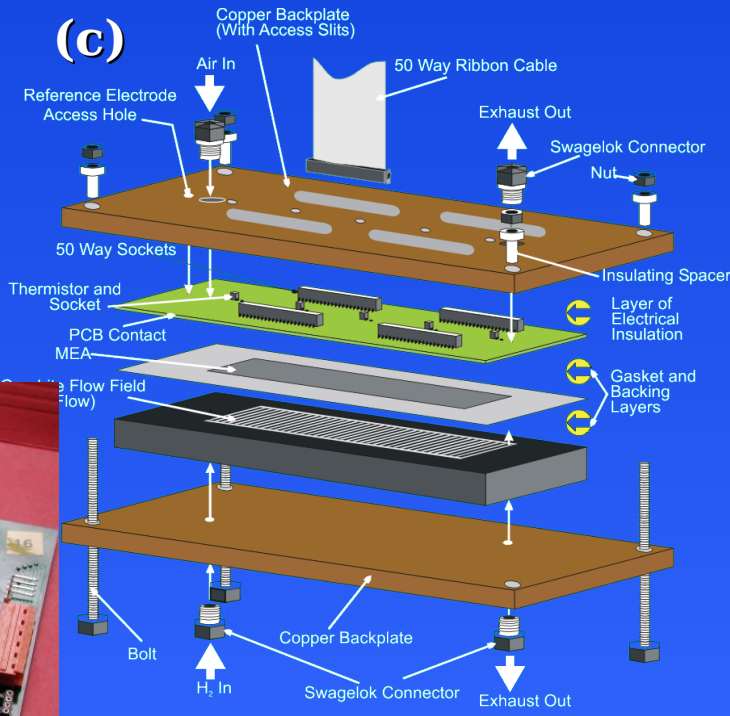
# New *in situ* techniques for studying and fuel cells

- Utilise a printed-circuit board, (a), to define electrical contacts to the unsegmented MEA, (b);
- MEA and circuitboard are assembled into a fuel cell, (c);
- Each contact is controlled by its own load, (d); A rack of loads required to control the

(a)

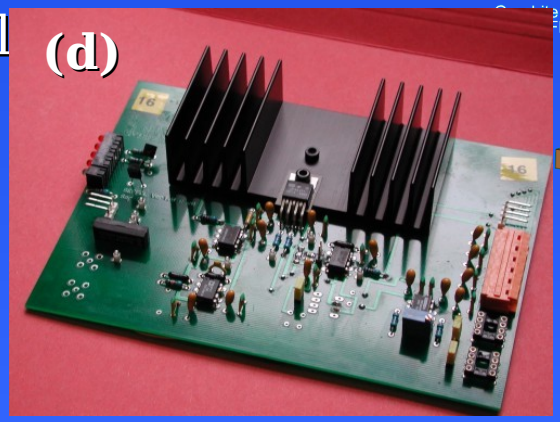
(b)

(c)



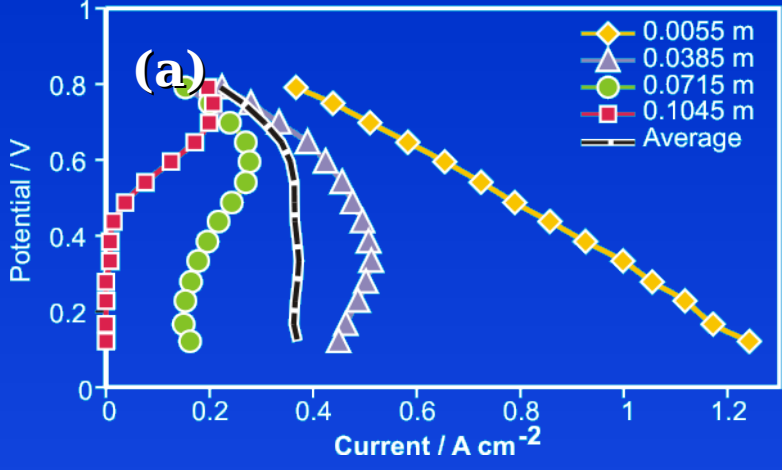

(e)

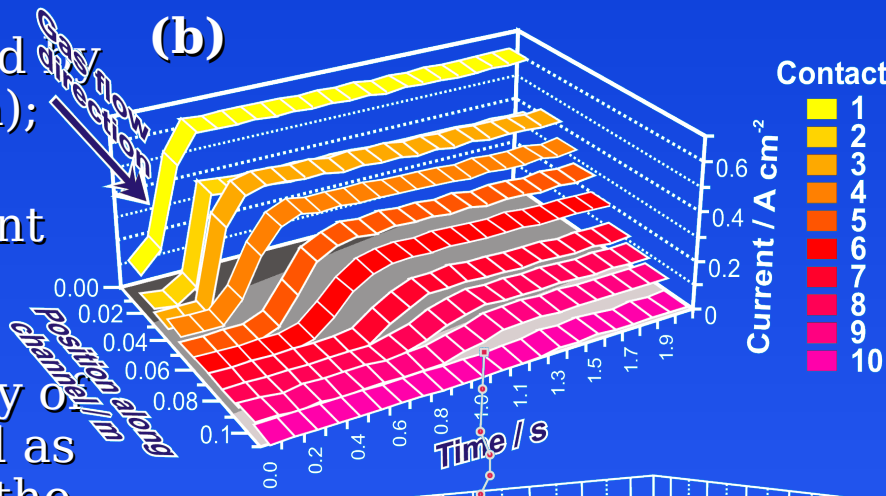
(d)

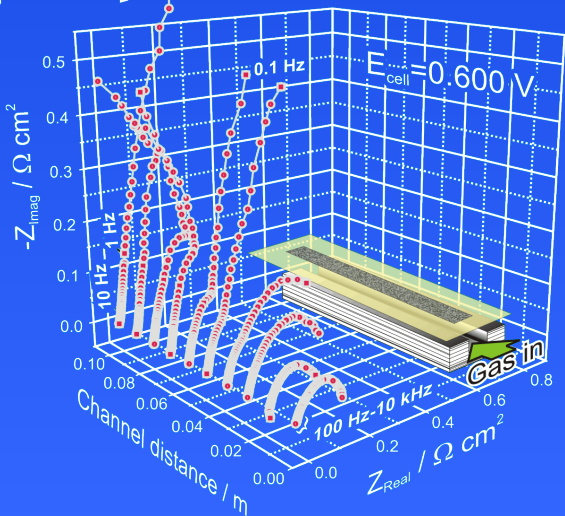


# New *in situ* techniques for studying and fuel cells -results

- IV curves are dependent upon position in channel with the local current being influenced by what happens 'up-stream', (a);
- The instrument is capable of resolving the real-time current response, (b);
- Localised impedance measurements allow a variety of parameters to be determined as a function of position within the fuel cell, (c).





**References**

1. Daniel J. L. Brett, Stephen Atkins, Nigel P. Brandon, Velisa Vesovic, Nikos Vasileiadis and Anthony R. Kucernak, "Measurement of the current distribution along a single flow channel of a solid polymer fuel cell", *Electrochem. Comm.*, 3(2001), pp. 628-632
2. Daniel J. L. Brett, Stephen Atkins, Nigel P. Brandon, Velisa Vesovic, Nikos Vasileiadis and Anthony R. Kucernak, "Localised Impedance Measurements along a Single Channel of a Solid Polymer Fuel